PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

New Fluorination Process

We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York, United States of America, of 61, Broadway, New
5 York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and
10 by the following statement: —

THIS INVENTION relates to the fluorination of 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane, $CF_3CFClCFCl_2$, b.p. 73—74° C., and to the preparation of 1,2-dichloro-
15 1,1,2,3,3,3-hexafluoropropane, $CF_3CFClCF_2Cl$, b.p. about —35° C.

1,2 - dichloro - 1,1,2,3,3,3 - hexafluoropropane is useful as a solvent, a heat transfer medium, a dielectric material, and as an inter-
20 mediate for manufacture of refrigerants and perfluoropropene.

It has been proposed to make 1:2-dichlorohexafluoropropane by the liquid phase reaction of a chlorofluoropropane and an antimony
25 chlorofluoride fluorinating agent at relatively high temperature and high pressure in a sealed bomb. Such a procedure is obviously uncommercial. Moreover, fluorination reactions of the general type to which the inven-
30 tion relates have been effected by means of powerful fluorinating agents such as cobaltic fluoride. Fluorinations of this nature necessitate separate stage refluorination of the fluorinating agent with elemental fluorine, the
35 use of which constitutes a self-evident disadvantage.

The present invention provides a process for making 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane by the fluorination of 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane which can be
40 carried out continuously at relatively low temperatures and at substantially atmospheric pressure. The new process moreover avoids disadvantages inherent in processes involving use of sealed bombs or elemental fluorine.
45 According to the present invention a process for making 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane comprises subjecting 1,1,2-trichloro - 1,2,3,3,3 - pentafluoropropane to the action of gaseous substantially anhydrous
50 hydrogen fluoride, in the gas phase, at substantially atmospheric pressure and a temperature not substantially higher than 150° C., and in the presence of a solid, activated carbon-pentavalent antimony fluoro–chloride
55 catalyst in which the antimony halide component has a composition corresponding to $Sb F_x Cl_{5-x}$ in which x is at least equal to 2 but less than 5.

Thus in a typical procedure gaseous 1,1,2-
60 trichloro - 1,2,3,3,3 - pentafluoropropane and gaseous anhydrous hydrogen fluoride are continuously metered, mixed and fed into a tubular reactor which is packed, preferably full, of solid, activated carbon-antimony
65 fluorochloride catalyst and which may be made of inert material such as nickel "Monel", (Registered Trade Mark) or "Inconel" (Registered Trade Mark), and enveloped in a suitable tubular electric furnace
70 provided with automatic heating to maintain the desired reaction zone temperature. The reaction involved in the invention may be represented by

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$$CF_3CFClCFCl_2 + HF \longrightarrow CF_3CFClCF_2Cl + HCl.$$
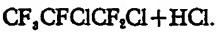
Product recovery may be effected by methods conventional in this art. For example, the products leaving the reaction zone may be passed through scrubbers to remove hydrogen fluoride and hydrogen chloride, and the
80 material leaving the scrubbers may be dried, and then totally condensed in a receiver by suitable cooling, such as that obtained by

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the use of a dry ice-acetone mixture. The resulting condensate may then be fractionally distilled in suitable equipment for recovery of the desired product, and separation of unreacted materials which may be recycled.

The catalyst may be made by impregnating activated carbon with pentavalent antimony fluorochloride. The activated carbons which may be used are granular materials readily available from several commercial sources. Suitable materials are various grades of about 8—14 mesh activated carbon, such as Columbia 6G, Columbia SW and "Darco" (Registered Trade Mark). The granular size of the activated carbon employed is not highly critical. Ordinarily, the reaction is carried out in elongated tubular reactors and in these instances it is desirable to employ in the catalyst activated carbon granules of average mesh size between 1/20 and 1/4, or better 1/8 to a 1/10, of the reactor diameter.

Incorporation of pentavalent antimony fluorochloride into the activated carbon may be accomplished in various ways. For example, the carbon granules may be impregnated, for example by soaking, with an aqueous solution of either antimony trichloride or antimony trifluoride, dried by heating to remove water, and the trivalent antimony converted to penavalent by passing chlorine through the material at about 50—100° C. Another method of catalyst preparation includes impregnation of activated carbon granules with a volatile, organic, non-reactive solvent containing dissolved antimony pentachloride or antimony trichloride, the solvent being for example a fluorinated hydrocarbon such as 1,1,2-trichloro-1,2,2-trifluoroethane for antimony pentachloride, or carbon disulphide for antimony trichloride. The mass may be dried by heating to remove the solvent and trivalent antimony (when present) converted to the pentavalent form by treatment with chlorine, at e.g. 50—100° C. In situations in which a greater antimony fluorochloride loading of the activated carbon is desired, liquid antimony pentachloride may be slowly poured into the top of a column of activated carbon, and permitted to percolate down through the column. Excess liquid antimony pentachloride is drained from the column by gravity. Following impregnation of the activated carbon granules, and subsequent to conversion where necessary, of all the antimony to antimony pentachloride, the impregnated carbon may be gassed with hydrogen fluoride at, for example, 40—115° C. to convert the antimony pentachloride to pentavalent antimony chlorofluoride.

The relative proportions of activated carbon and pentavalent antimony fluorochloride in the finished solid catalyst may vary considerably. Generally, the finished catalyst preferably contains at least about 25% by weight of carbon. Whatever method for making the catalyst is employed, the procedure and the relative amounts of activated carbon and antimony halide should ordinarily be regulated so that the amount of pentavalent antimony fluorochloride incorporated with the activated carbon is such as to provide in the finished catalyst at least 10% by weight of antimony (expressed as Sb). The weight content of antimony (expressed as Sb) may vary from 10% up to about 35%, preferably being 20 to 30%.

The composition of the pentavalent antimony fluorochloride component of the finished catalyst may likewise be varied to some extent. The composition can be adjusted by the degree of treatment with hydrogen fluoride of the mass comprising activated carbon and antimony pentachloride. As already stated, the composition of the pentavalent antimony fluorochloride component of the finished catalyst may be represented by the formula SbF_xCl_{5-x}, and the treatment with hydrogen fluoride should be regulated so that x is at least equal to two but less than five, preferably at least three but less than five.

When 1,1,2 - trichloro - 1,2,3,3,3 - pentafluoropropane and anhydrous hydrogen fluoride have been charged into the reactor, significant reaction proceeds at any temperature high enough to maintain the organic starting material and hydrogen fluoride both in the gas phase. Ordinarily, it is preferred to maintain the reactor temperature at not less than about 90° C. As noted, the above described catalyst initiates reaction of the said organic starting material and hydrogen fluoride at remarkably low temperatures, and the reaction zone temperature should be not substantially higher than 150° C. Usually, temperatures as high as about 150° C. afford no particular advantage, and it is preferred to maintain the reaction zone temperature not higher than about 130° C., and preferably at 90—130° C.

The theoretically required mol ratio of hydrogen fluoride to organic starting material is approximately 1:1: Less than theoretical quantities of hydrogen fluoride may be employed, but to no advantage, and such proportion of reactants is not preferred. Preferably molecular excesses of hydrogen fluoride are utilized, and while such mol ratios of hydrogen fluoride: organic starting material may, for example, lie in the range of 1:1 to 5:1, they are preferably from 2:1 to 4:1.

During the course of the reaction a relatively small amount of free chlorine may be fed into the reactor with the hydrogen fluoride and organic starting material, to maintain the antimony halide catalyst in the pentavalent form. The quantity of chlorine so charge may vary from 0.1 to 0.5 mols of chlorine per mol of hydrogen fluoride charged.

As indicated above, the process may be carried out at substantially atmospheric pressure. It will be understood that in the practice of gas-phase catalytic processes of the general type described herein, i.e. processes in which a gas stream flows successively through reaction and product recovery systems, the pressure is considered for all practical purposes as being substantially atmospheric. Technically, however, pressures in such systems are sufficiently on the positive side to cause commercially satisfactory gas flow through the apparatus train. Thus, strictly speaking, depending upon factors such as apparatus design, mesh size of catalyst, unpacked gas space in the reactor, desired contact time, etc., actual pressures in systems of the kind under consideration may vary from 0.14 up to say 0.7—1.05 kg./sq. cm. gauge, and accordingly operations of this type are included in the designation of substantially atmospheric pressure.

Contact time may be varied considerably without noticeable falling off in process efficiency. Generally, increasing contact time and reactor temperature results in greater reaction. Significant conversions are effected with contact times as short as one second, but contact times may be as high as 120 seconds. Preferably, contact times lie in the range of 2 to 20 seconds. To a substantial extent, contact time, reactor temperature and ratio of reactants are inter-related, and depending upon apparatus and the particular operation at hand, optimum conditions as to contact time may be determined by test runs.

For product recovery the products of the reaction, which contain 1,2-dichloro-1,1,2,3,3,3 - hexafluoropropane, unreacted organic starting material, hydrogen fluoride and hydrogen chloride may be fed through a water scrub tower to remove the bulk of the hydrogen fluoride and hydrogen chloride from the gas stream. The latter, after discharge from the water scrubber, may be passed through a relatively weak, e.g. 10%, sodium hydroxide solution to remove traces of residual acid. After drying, by desiccants such as Drierite or calcium chloride, the dried gas stream then may be fed into a cold trap, refrigerated for example by a —78° C. dry ice-acetone mixture, and totally condensed. The condensate in the trap may then be suitably fractionally distilled to recover substantially pure 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane.

The following Example illustrates the invention.

EXAMPLE

In this run the activated carbon-pentavalent antimony fluorochloride catalyst was made in situ in the reactor. The latter consisted of a vertically mounted nickel pipe, 2.5 cms internal diameter and 91 cms long, enveloped in a cylindrical electric furnace. The lower end of the reactor was provided with connections for introduction of separately metered quantities of vaporous 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane, vaporous, substantially anhydrous hydrogen fluoride, and chlorine. At the outset, the reactor was packed with about 8—14 mesh Columbia 6G activated carbon. About 704 g. of liquid antimony pentachloride were fed into the top of the reactor. Unabsorbed surplus antimony pentachloride drained by gravity from the bottom of the activated carbon bed. The mass of activated carbon saturated with antimony penachloride was then gassed with anhydrous hydrogen fluoride at about 80—110° C. at a rate of about 2 mols/hr. for about 6 hrs. The amount of liquid antimony pentachloride fed into the reactor and the degree of absorption of the antimony halide by the activated carbon was such that the finished catalyst contained about 28% by weight of pentavalent antimony (expressed as Sb).

On completion of formation of the activated carbon-pentavalent antimony fluorochloride catalyst in the reactor, internal temperature in the reactor was brought up to about 115° C. and maintained at about this value throughout the fluorination of 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane. During a two hour period, about 283 g. (1.19 mols) of 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane were metered into the reactor at a rate of about 0.6 mol/hr.; about 81.0 g. (4.05 mols) of anhydrous hydrogen fluoride were metered into the reactor at a rate of about 2.03 mols/hr.; and about 35.0 g. (0.493 mol) of chlorine was fed into the reactor at a rate of about 0.247 mol/hr. The mol ratio of hydrogen fluoride to 1,1,2-trichloro - 1,2,3,3,3 - pentafluoropropane in the reactor feed was about 3.4:1. Contact time was about 3 seconds. Pressure in the reactor and recovery system was about 0.035—0.07 kg/sq.cm gauge, i.e. just sufficiently above atmospheric to effect flow of gas through the system. The materials leaving the reactor were passed into a conventional recovery train in which the reactor exit gas stream was water-scrubbed, scrubbed with aqueous NaOH, dried, and finally totally liquefied by condensation in a dry ice-acetone cooled trap at approximately —78° C. The total amount of organic substances condensed in the trap was about 218 g. On distillation of the condensate, there were recovered about 88.0 g. (0.398 mol) of 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane, $CF_3CFClCF_2Cl$, b.p. about —33° C.; and about 122 g. (0.514 mol) of 1,1,2 - trichloro - 1,2,3,3,3 - pentafluoropropane, $CF_3CFClCFCl_2$, b.p. about 73— 74° C. The reaction product thus contained about 44 mol % of the desired 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane, the remainder being unreacted 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane starting material. The

absence in the cold trap condensate of organic compounds other than 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane and unreacted starting material indicates a substantially 100% yield of desired product based on the starting material converted.

WHAT WE CLAIM IS:—

1. A process for making 1,2-dichloro-1,1,2,3,3,3 - hexafluoropropane which comprises subjecting 1,1,2 - trichloro - 1,2,3,3,3-pentafluoropropane to the action of gaseous substantially anhydrous hydrogen fluoride, in the gas phase, at substantially atmospheric pressure and a temperature not substantially higher than 150° C., and in the presence of a solid, activated carbon-pentavalent antimony fluorochloride catalyst in which the antimony halide component has a composition corresponding to Sb F_xCl_{5-x} in which x is at least equal to 2 but less than 5.

2. Process according to claim 1 in which the temperature is 90—130° C.

3. Process according to claim 1 or 2 in which the said catalyst contains at least about 25% by weight of activated carbon and at least 10% by weight of antimony (expressed as Sb).

4. Process according to any of claims 1 to 3 in which the said catalyst contains 20 to 30% by weight of antimony (expressed as Sb).

5. Process according to any one of the preceding claims in which x is at least 3 but less than 5.

6. Process according to any of claims 1 to 5 in which the mol ratio of hydrogen fluoride to 1,1,2-trichloro-1,2,3,3,3-pentafluoropropane is from 2:1 to 4:1

7. Process according to any of claims 1 to 5 in which the reaction is carried out in the presence of 0.1 to 0.5 mols of chlorine per mole of hydrogen fluoride.

8. Process according to any of claims 1 to 7 in which the reaction is carried out in a tubular reactor and the catalyst is in the form of granules having an average mesh size of an eighth to a tenth of the reactor diameter.

9. Process for making 1,2-dichloro-1,1,2,3,3,3-hexafluoropropane substantially as described.

10. 1,2 - Dichloro - 1,1,2,3,3,3 - hexafluoropropane when made by the process of any of the preceding claims.

J. A. KEMP & CO.,
Chartered Patent Agents,
14, South Square, Gray's Inn,
London, W.C.1.